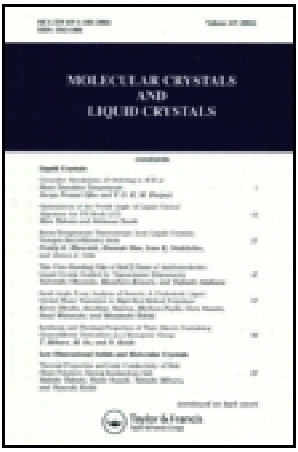
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 11:06
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Mesomorphic Investigations of Liquid Crystalline Compounds Having a Benzothiazole Ring

B. T. Thaker [a], N. J. Chothani [a], B. S. Patel [a], Y. T. Dhimmar [a], D. B. Solanki [a], Neeraj Patel [a], K. B. Patel [a] & U. Makawana [a]

[a] Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat, India

Published online: 22 Apr 2013.

To cite this article: B. T. Thaker, N. J. Chothani, B. S. Patel, Y. T. Dhimmar, D. B. Solanki, Neeraj Patel, K. B. Patel & U. Makawana (2013) Synthesis and Mesomorphic Investigations of Liquid Crystalline Compounds Having a Benzothiazole Ring, Molecular Crystals and Liquid Crystals, 575:1, 64-76, DOI: 10.1080/15421406.2013.766947

To link to this article: http://dx.doi.org/10.1080/15421406.2013.766947

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 575: pp. 64–76, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.766947

Synthesis and Mesomorphic Investigations of Liquid Crystalline Compounds Having a Benzothiazole Ring

B. T. THAKER,* N. J. CHOTHANI, B. S. PATEL,
Y. T. DHIMMAR, D. B. SOLANKI, NEERAJ PATEL,
K. B. PATEL, AND U. MAKAWANA

Department of Chemistry, Veer Narmad South Gujarat University, Surat,
Gujarat, India

Two homologous series of calamitic liquid crystals containing a benzothiazole ring and two different linkages have been prepared, and their liquid crystalline properties are studied and compared with each other and those of similar structure. The mesogens with only the cinnamate linking group showed better thermal properties than those with an ester. Nematic and smectic phases were observed. All the compounds of both the series were characterized by elemental analysis, FT-IR, mass spectrometry, ^{1}H-NMR, and ^{13}C-NMR. Phase transition temperatures and the thermal parameters were obtained from differential scanning calorimetery (DSC). The textural observations were performed using hot-stage Polarizing Optical Microscopy (POM).

Keywords 6-Fluorobenzothiazole; azomesogens; cinnamate; enantiotropic; nematic; SmA

1. Introduction

We recently reported the synthesis and characterization of a three-ring heterocyclic mesogen incorporating the thiophene ring, and the bent nature of the molecule gave fairly low melting points and an extensive nematic phase [1]. The introduction of a fluoro substituent to mesogens often affords liquid crystals with modified physical properties [2]. Many liquid crystals have fluorinated aromatic rings [3–6], and fluorinated ferroelectric liquid crystals have a large spontaneous polarization and a low viscosity, which can improve the response time of the liquid crystal for switching [7–11].

The study of heterocyclic liquid crystal compounds has dramatically increased in recent years due to their wider range of optical and photochemical properties. The growing scientific interest in the synthesis of heterocyclic-based liquid crystals has prompted us to synthesize a series of 6-fluorobenzothiazole liquid crystals. Compounds containing benzothiazole and benzoxazole rings have been studied as they exhibit interesting fluorescent and photophysical properties [12,13]. A nematic benzothiazole was first reported by Vorlander and Weisswange [14]. Ha et al. reported similar compounds based on benzothiazole units containing ester and Schiff base as linking groups [15]. Nematic and/or smectic

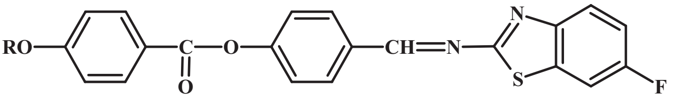
---

*Address correspondence to B. T. Thaker, Department of Chemistry, Veer Narmad South Gujarat University, Surat- 395007, Gujarat, India. Tel.: +91-9228377618. E-mail: btthaker1@yahoo.co.in

C mesophases formed by these rod-like compounds were observed. In addition, a number of benzothiazole-derived compounds were found to exhibit interesting photophysical and fluorescent properties by Iwata et al. [16] and Gallas et al. [17]. Pavluchenko et al. [18] reported liquid crystals containing benzothizole and benzoxazole rings with different central linkages and different lateral substitution at different positions so as to evaluate the effect of structural changes on mesomorphic properties. They observed that the substitution at sixth position was thermally more stable as compared to that of the fifth position on the benzothiazole ring.

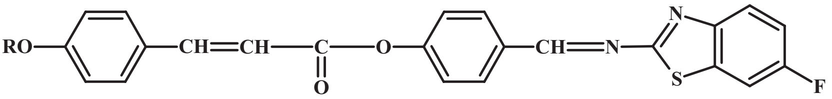
As part of our continuing studies of heterocyclic mesogens, in this paper, we describe the synthesis, characterization, and mesomorphic properties of a two series of calamitic benzothiazole derivatives. The present work describes a comparative study of the influence of the linkage group on the mesomorphism of the materials. The influence of the terminal fluoro substituent on the mesomorphic properties is discussed through the comparison with known liquid crystals of similar structure. The structures of the two novel series of liquid crystals (**A** and **B**) are shown below.

Series-A



Where R = C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16, 18

Series-B



Where R = C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16, 18

2. Experimental Details

2.1 Materials

4-hydroxybenzoic acid and 4-hydroxy benzaldehyde were obtained from Merck, Germany, alkyl bromides were purchased from Lancaster, England; malonic acid was purchased from Fluka Chemie, Switzerland; *N,N'*-dicyclohexylcarbodiimide (DCC) and dimethyl amino pyridine (DMAP) were purchased from Acros Organics, USA; 4-fluoroaniline was provided by Aarti Chemical [P] Ltd., Vapi and used without further purification. Bromine, potassium thiocyanate, pyridine, piperidine, anhydrous potassium carbonate, acetone, ethanol, methanol, acetic acid, ethyl acetate, HCl, KOH, NaOH, NH_4OH, etc. were used as received. Column chromatography employed Acme's Silica Gel (100–200 mesh). Solvents were dried and distilled prior to use.

2.2 Measurements

Elemental analysis (C, H, N) was performed using a thermo Scientific FLASH 2000 instrument at G.N.F.C. (Gujarat Narmada Valley Fertilizer Company Ltd., Bharuch). Infrared spectra were recorded using a Thermo Scientific Nicolet iS-10 spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr discs. High resolution (400 MHz) NMR Spectra of the mesogenic compounds were recorded at room temperature as a 15%–20% solution in $CDCl_3$ using TMS as internal standard on a Bruker Avance II 400 NMR spectrometer at SAIF (Sophisticated Analytical Instrument Facilities), Panjab University, Chandigarh. Mass spectra (TOF MS ES+) of the compounds were recorded using a Finnigan MAT-8230 Mass Spectrometer at SAIF (Sophisticated Analytical Instrument Facilities), Panjab University, Chandigarh. Thin-layer chromatography (TLC) analyses were performed using aluminium-backed silica-gel plates (Merck60 F524) and examined under shortwave UV light. Thermal (DSC) analyses of the liquid crystalline compounds were carried out by Atul industries Ltd. P.P site Atul. DSC analyses were performed on a Mettler M-3 thermo balance (Switzerland) with microprocessor TA-300 instrument at a heating rate of 10°C/min in a N2 atmosphere. The optical microscopy studies were determined by using polarizing microscope Nikon Eclipse 50i POL (Japan) equipped with Linkam Analysa-LTS420 hot stage (London) at our department as standard procedure.

2.3 Synthesis of Series-A and -B Compounds

The synthetic route to Series-A and B is illustrated in Scheme 1.

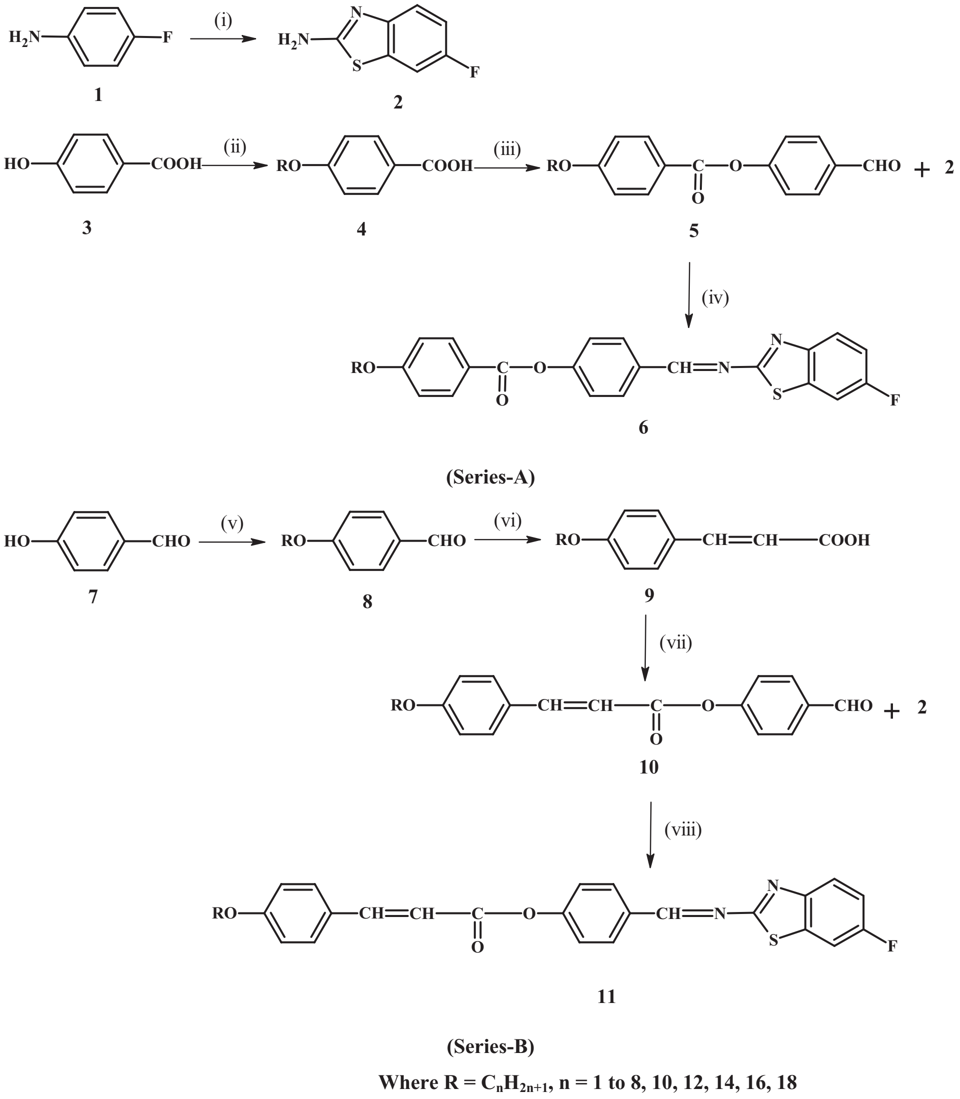
2.3.1 2-Amino-6-fluorobenzothiazole ***(2)***. 2-Amino-6-fluorobenzothiazole **(2)** was prepared from 4-fluoroaniline **(1)** by the reported method [19]. The resulting compound was crystallized from 1:1 aqueous ethanol to afford pure pale yellow needles of **(2)**. Yield: 87%. Clearing Point: 184°C.

2.3.2 4-n-Alkoxybenzoic Acids ***(4)***. 4-*n*-Alkoxybenzoic acids **(4)** were synthesized by the modified method of Dave and Vora [20]. The melting point and clearing point of these compounds were compared with those reported, and they are similar to reported values [21].

2.3.3 4-(4′-n-Alkoxy benzoyloxy) Benzaldehydes ***(5)*** *[22,23].* These compounds were prepared by esterification of a stirred mixture of the appropriate compound **1** (2.22 m mol) and 4-hydroxybenzaldehyde (0.271 g, 2.22 mmol), *N,N′*-dicyclohexylcarbodiimide (DCC) (0.455 g, 2.22 mmol), dimethyl amino pyridine (0.024 g, 0.2 mmol), and dry CH_2Cl_2 (20 mL) at room temperature overnight under an inert N_2 atmosphere. The ensuing white precipitate was isolated by Buchner filtration and discarded, while the filtrate was evaporated to dryness in vacuum. The resultant crude residue was purified by column chromatography on silica gel eluting with dichloromethane, followed by repeated recrystallization from ethanol until constant transition temperatures were achieved.

2.3.4 6-Fluoro 2-[4-(4′-n-Alkoxy benzoyloxy) Benzylidenamino] Benzothiazole (Series-A). 2-Amino-6-fluorobenzothiazole **(2)** (0.721 g, 4 mmol) and 4-(4′-*n*-alkoxybenzoyloxy) benzaldehydes **(5)** (4 mmol) were refluxed for 3 h in an ethanol solution (60 mL) upon the addition of two drops of acetic acid as catalyst. The reaction mixture was then filtered and the filtrate was left to evaporate at room temperature in the fume hood. The yellow solid was obtained and it was recrystallized from ethanol and used for further reaction. The crude product was purified by column chromatography (silica gel, $CHCl_3$/EtOAc 9/1).

2.3.5 General Synthesis of 4-n-Alkoxy benzaldehydes ***(8)****, 4-n-Alkoxy Cinnamic Acids* ***(9)*** *and 4-(4-n-alkoxycinnamoyloxy) Benzaldehydes* ***(10)***. 4-*n*-Alkoxy benzaldehydes **(8)** and



Scheme 1. Synthetic route to Series-I and -II. Reagents and conditions: **(i)** KSCN, Br_2, AcOH; **(ii)** RBr, KOH, Ethanol; **(iii)** DCC, DMAP, CH_2Cl_2, 4-hydroxy benzaldehyde stirred at 0°C for 1 h, stirred at room temperature for 24 h; **(iv)** Ethanol, 2–3 drop AcOH reflux for 4 h; **(v)** RBr, K_2CO_3, Dry acetone; **(vi)** Malonic acid, pyridine, pipyridine, reflux; **(vii)** DCC, DMAP, CH_2Cl_2, 4-hydroxy benzaldehyde stirred at 0°C for 1 h, stirred at room temperature for 24 h; **(viii)** Ethanol, 2–3 drop AcOH reflux for 4 h.

4-*n*-alkoxycinnamic acids **(9)** were prepared by the method of Gray and Jones [21]. Also, 4-(4-*n*-alkoxy cinnamoyloxy) benzaldehydes **(10)** was prepared by following the procedure described for the compounds of Series-A **(2.3.3)**. Here, 4-*n*-alkoxy cinnamic acids were used instead of 4-*n*-alkoxy acid as in Series-A.

2.3.6 6-Fluoro 2-[4-(4′- n-Alkoxy Cinnamoyloxy) benzylidenamino] Benzothiazole (Series-B). The Schiff's bases of Series-B were synthesized by condensing equimolar quantities of appropriate 4-(4-*n*-alkoxy cinnamoyloxy) benzaldehydes **(10)** (4 mmol) with 2-amino-6-fluorobenzothiazole **(2)** (0.721 g, 4 mmol) in boiling ethanol. The reaction mixture was refluxed for 1–2 h with 2–3 drops of acetic acid. The reaction mixture was kept overnight. The yellow solid product was purified by column chromatography (silica gel, $CHCl_3$/EtOAc 9/1). The Schiff's bases of the Series-B were crystallized from ethanol until constant transition temperatures were obtained.

2.4 Data

2.4.1 6-Fluoro 2-[4-(4′-tetradecanoyloxybenzoyloxy) benzylidenamino] benzothiazole. **Yield** 73%. **Clearing Point:** 144°C, **UV($CHCl_3$)** λmax: 556 nm, Found C, 71.55; H, 6.83; N, 4.51; Calc. for $C_{35}H_{41}N_2SO_3F$ (588 g/mol); C, 71.42; H, 6.97; N, 4.76;%. **IR (KBr)** υmax cm^{-1} 3065 (C–H Str. aromatic), 2925, 2853 (C–H Str. aliphatic), 1734 (C=O Str. ester), 1642 (CH=N, Str. azomethine) 1475, 1362, 1065 (benzothiazole), 882, 848, 638 (C–S–C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ/ppm 0.86–0.89 (t, CH_3), 1.26–1.91 (m, CH_2), 4.03–4.06 (t, OCH_2), 6.97–8.12 (m, Ar–H), 8.54 (s, CH=N). **^{13}C NMR ($CDCl_3$):** δ/ppm 14.03 ($\underline{C}H_3$), 24.83–33.51 ($\underline{C}H_2$) 68.42 ($O\underline{C}H_2$), 115.20–163.91 (Ar–$\underline{C}$), 164.29 (–$\underline{C}$H=N), 171.37 (–$\underline{C}$=O–), TOF MS ES+ m/z (rel.int%): 588 $(M)^+$ m/z.

2.4.2 6-Fluoro 2-[4-(4′-tetradecanoyloxycinnamoyloxy) benzylidenamino] benzothiazole. **Yield** 75%. **Clearing Point:** 195°C, **UV ($CHCl_3$)** λmax: 566 nm, Found C, 72.55; H, 6.83; N, 4.43; Calc. for $C_{37}H_{43}N_2SO_3F$ (614 gm/mole); C, 72.31; H, 7.00; N, 4.56;%. **IR (KBr)** υmax cm^{-1} 3091 (C–H Str. aromatic), 2973, 2880 (C–H Str. aliphatic), 1731 (C=O Str. ester), 1635 (CH=N, Str. azomethine) 1478, 1364, 1069 (Benzothiazole), 881, 850, 636 (C–S–C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ/ppm 0.86–0.90(t, CH_3), 1.22–1.91 (m, CH_2), 3.98–4.08(t, OCH_2), 6.94–7.97 (m, Ar–H), 8.53 (s, CH=N). **^{13}C NMR ($CDCl_3$):** δ/ppm 14.13 ($\underline{C}H_3$), 24.76–33.30 ($\underline{C}H_2$) 68.26 ($O\underline{C}H_2$), 114.04–161.67 (Ar–$\underline{C}$), 165.08 (–$\underline{C}$H=N), 169.91 (–$\underline{C}$=O–), 115.01; 147.40 (–$\underline{C}$H=$\underline{C}$H–). TOF MS ES+ m/z (rel.int%): 615 $(M+1)^+$ m/z.

3. Results and Discussion

The synthesis of Series-A and -B is shown in Scheme 1. All compounds were characterized by elemental analysis, UV/Visible, FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy. The mesomorphic properties of all the synthesized compounds have been characterized by differential scanning calorimetry (DSC) and polarizing optical microscope (POM) attached with a Linkam hot stage. The thin-film samples were obtained by sandwiching them a glass slide and cover slip.

3.1 Thermal and Phase Behavior

All the compounds synthesized in Series-A exhibit an enantiotropic nematic phase. The SmC mesophase commences from the *n*-octyloxy derivative. The *n*-octyloxy and *n*-decyloxy compounds are monotropic and the *n*-dodecyloxy to *n*-octadecyloxy($C_{12,}$ $C_{14,}$ $C_{16,}$ $C_{18,}$) members exhibit an enantiotropic SmC phase. The enantiotropic SmC mesophase is obtained from the *n*-dodecyloxy derivative and persists up to the *n*-octadecyloxy derivative. The transition temperatures are recorded in Table 1 and a plot of transition temperatures against the number of carbon atoms in the alkoxy chain in Fig. 1 shows a steady fall in the temperature of nematic isotropic transitions. The trend exhibits a marked odd-even effect in

Table 1. Transition temperature (°C) data of 6-fluoro 2-[4-(4′-n-alkoxy benzoyloxy)benzylidenamino]benzothiazole (Series-A)

		Transition temperature (°C)						
Compounds	$R = n$ alkoxy	Cr		SmC		N		I
A_1	Methyl	●	–	–	165	●	208	●
A_2	Ethyl	●	–	–	157	●	203	●
A_3	Propyl	●	–	–	160	●	197	●
A_4	Butyl	●	–	–	148	●	194	●
A_5	Pentyl	●	–	–	142	●	192	●
A_6	Hexyl	●	–	–	130	●	183	●
A_7	Heptyl	●	–	–	119	●	176	●
A_8	Octyl	●	(57)[a]	●	102	●	165	●
A_{10}	Decyl	●	(61)[a]	●	91	●	158	●
A_{12}	Dodecyl	●	64	●	78	●	152	●
A_{14}	Tetradecyl	●	66	●	76	●	144	●
A_{16}	Hexadecyl	●	70	●	79	●	139	●
A_{18}	Octadecyl	●	77	●	86	●	145	●

[a] Monotropic.

crystal-mesophase transition temperatures for the lower member of homologues series, and as the number of carbon atoms increases the odd-even effect is not so pronounced. There is also a tendency for rising smectic-nematic transition temperatures in the ascending series.

The graph of phase transition temperatures against the number of carbons in the alkanoyloxy chain enables the effect of the terminal chain on the mesomorphic properties to be established (Fig. 1). The adequate geometric anisotropy (ratio between length and

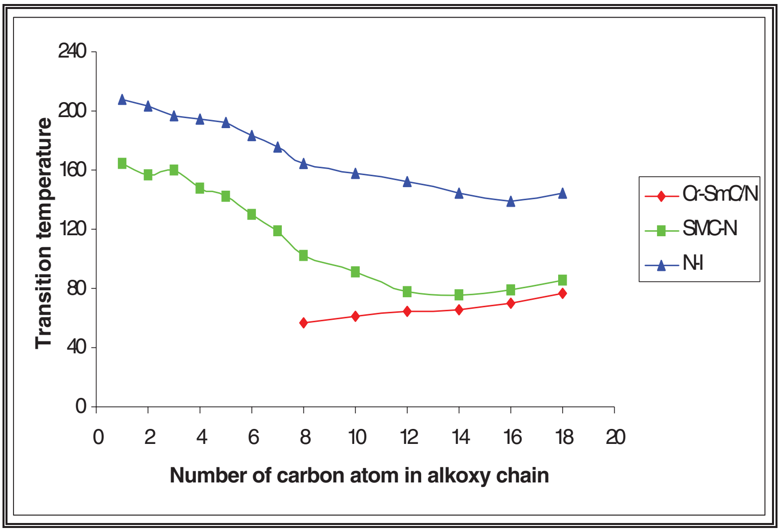


Figure 1. Transition temperature curve of Series-A.

Table 2. Transition temperature (°C) data of 6-fluoro 2-[4-(4′- n-alkoxy cinnamoyloxy) benzylidenamino] benzothiazole (Series-B)

		Transition temperature (°C)						
Compounds	$R = n$ alkoxy	Cr		SmC		N		I
B_1	Methyl	•	–	–	179	•	223	•
B_2	Ethyl	•	–	–	176	•	217	•
B_3	Propyl	•	–	–	165	•	212	•
B_4	Butyl	•	–	–	153	•	209	•
B_5	Pentyl	•	–	–	142	•	205	•
B_6	Hexyl	•	–	–	135	•	203	•
B_7	Heptyl	•	–	–	129	•	201	•
B_8	Octyl	•	–	–	124	•	199	•
B_{10}	Decyl	•	(117)[a]	•	126	•	198	•
B_{12}	Dodecyl	•	108	•	133	•	196	•
B_{14}	Tetradecyl	•	101	•	122	•	195	•
B_{16}	Hexadecyl	•	103	•	119	•	189	•
B_{18}	Octadecyl	•	106	•	115	•	182	•

[a] Monotropic.

width of the molecule) is an important point. Based on Fig. 1, in Series-A, as the length of the carbon chain increased, a monotropic (metastable) SmC phase was observed for the C_8 derivative. When the carbon chain reached C_{12}, the enantiotropic (stable) SmC phase was observed, which accompanied the nematic phase at a higher temperature was induced. The nematic transition temperature shows a descending trend from the C_1 to C_2 members and then gradually increases from the C_3 and higher members. As the alkyl chain gets longer, the temperature continued to decrease from C_3 to C_{14} members. Due to the excessive van der Waals attractive forces between the long alkyl chains, the melting temperatures increased obviously from C_{14} to C_{18} members [24]. Likewise, clearing points then descended with the increase in length of the carbon chain due to the dilution of the mesogenic core, resulting from the flexibility provided by the terminal alkanoyloxy chain [25]. A clear increment was observed when moving to the longest chain member (C_{18}). By referring to the graph, the nematic phase range.

All the thirteen members of Series-B exhibit an enantiotropic nematic phase. The SmC phase commences from the *n*-decyloxy derivative as a monotiotropic mesophase, the enantiotropic mesophase is seen from the *n*-dodecyloxy derivative and remains up to the *n*-octadecyloxy derivative. The transition temperatures are recorded in Table 2 and a plot of transition temperatures against the number of carbon atoms in the alkoxy chain is given in Fig. 2. It can be seen that the crystal to mesophase transition temperatures decrease with the increase in the length of terminal alkoxy tail. The nematic-isotropic transition temperatures also decrease with an increase in the number of carbon atoms in the alkoxy chain, whereas it exhibits a tendency for rising SmC-nematic transition temperature in ascending series, which levels off slightly in the higher homologues. In Series-B, as the length of the carbon chain increased, a monotropic (metastable) SmC phase was observed for the C_{10} derivative. Once the carbon chain reached C_{12}, the enantiotropic (stable) SmC phase is observed, which accompanies the nematic phase at a higher temperature. The

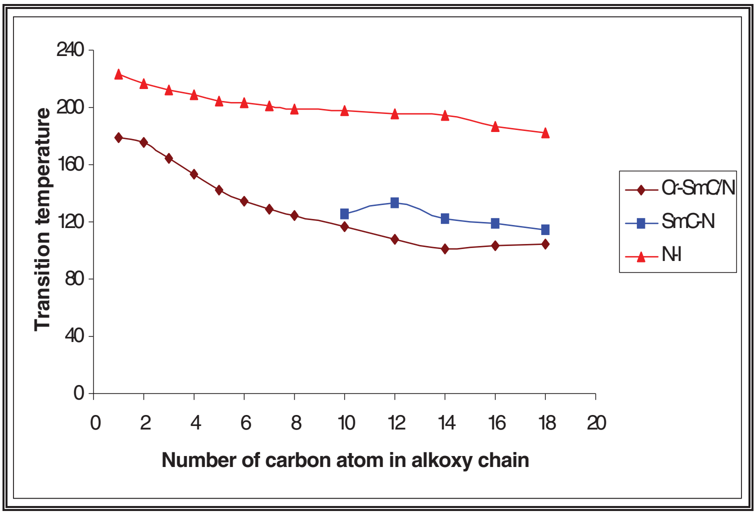


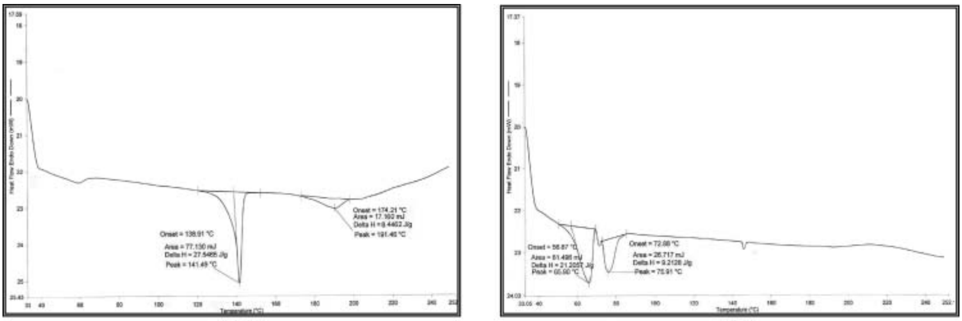
Figure 2. Transition temperature curve of Series-B.

nematic transition temperature shows a descending trend from the C_1 to C_{12} members and then gradually increases from the C_{14} members. Clearing points then descended with the increase in length of the carbon chain due to the dilution of the mesogenic core resulting from the flexibility provided by the terminal alkanoyloxy chain.

DSC is a valuable method for the detection of phase transitions. It yields quantitative results. The phase transition temperatures and corresponding enthalpy changes of compounds A_5, A_{14}, B_5, and B_{14} were determined using a DSC. The data obtained from the DSC analysis are summarized in Table 3, which helps further to confirm the mesophase type. Table 3 shows the phase transition temperature, associated enthalpy (ΔH), and molar entropy ΔS for compounds of Series-A (A_5, A_{14},) and Series-B (B_5, B_{14}). The DSC curves of representative compounds are shown in Figs 3 and 4. Microscopic transition temperature values are similar to the DSC data.

Table 3. DSC data of the Series-A and B

Series	Compounds No.	Transition	Peak/(POM) Temp. (°C)	ΔH Jg^{-1}	ΔS $Jg^{-1}K^{-1}$
A	A_5	Cr-N	141.49 (142.8)	27.54	0.1946
		N-I	191.46 (192.2)	8.44	0.0440
	A_{14}	Cr-SmC	65.90 (66.6)	21.20	0.3216
		SmC-N	75.91 (76.2)	9.21	0.1212
		N-I	144.0 (144.1)	—	—
B	B_5	Cr-N	141.66 (142.8)	12.18	0.0859
		N-I	204.57 (205.8)	3.51	0.0171
	B_{14}	Cr-SmC	100.92 (101.1)	3.79	0.0375
		SmC-N	121.41 (122.4)	11.19	0.0921
		N-I	194.75 (195.7)	14.31	0.0734



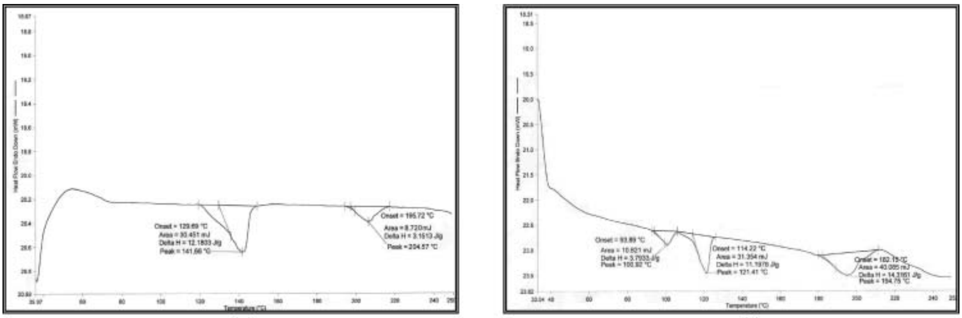
(a) (b)

Figure 3. (a) DSC thermogram for compound no. 5 (Series-A) and (b) DSC thermogram for compound no. 14 (Series-A).

3.2 Structure-Mesomorphic Property Relationships

Table 4 summarizes the average thermal stabilities and comparative geometry of the present Series-A, -B and the structurally related Series-I [26], −II [27] and –III [28]. The smectic as well as nematic thermal stabilities of Series-A are much lower than those of Series-B. The average smectic mesophase range of Series-B is higher by 1.6°C and the nematic mesophase range is higher by 3.4°C compared to the respective mesophase ranges of Series-A. The molecules of Series-B have a cinnamoyloxy (–CH=CH–COO–) central linkage, while Series-A have an ester (–COO) central linkage. The mesomorphism results can be attributed to the greater length and higher polarizability of Series-B molecules.

Reference to Table 4 indicates that the smectic and nematic thermal stabilities of Series-A compounds are higher than those of Series-I. Compared with molecules of Series-I the molecules of Series-A are a little longer and more polarizable. Although smectic phase stability is enhanced from the C_{12} to C_{18} members, the increasing melting temperatures cause the SmC phase to become significant. The smectic phase can be only observed in both the series for the mid to long chain derivatives.



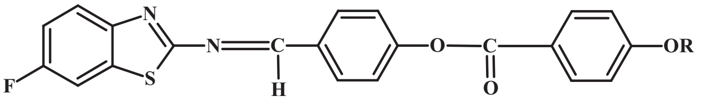
(a) (b)

Figure 4. (a) DSC thermogram for compound no. 5 (Series-B) and (b) DSC thermogram for compound no. 14 (Series-B).

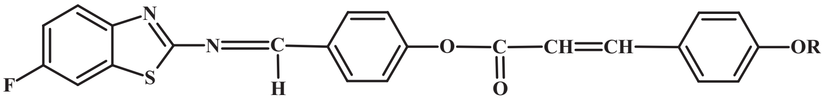
Table 4. The mesophase range and thermal stabilities of Series-A, -B and structurally related Series I, II, and III

Series	Mesophase range		Thermal stabilities		Commencement of smectic phase
	Smectic	Nematic	Smectic	Nematic	
A (C_{10}–C_{18})	14.4	65.6	67.6	82.00	C_8
B (C_{10}–C_{18})	16.0	69.0	107.0	123.00	C_{10}
I (C_{10}–C_{18})	6.36	30.9	75.04	81.5	C_{10}
II (C_8–C_{16})	45	55.60	101.00	146.00	C_7
III (C_8–C_{16})	58.00	63.60	90.20	148.2	C_8

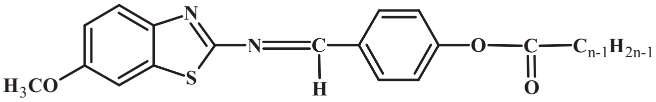
Table 4 shows that both Series-A and I exhibit an enantiotropic nematic mesophase. Mesophase length and nematic thermal stability of Series-A are higher by 34.7°C and 0.5°C, respectively, than that of Series-I because of the greater length of Series-A provided by the additional aromatic ring.



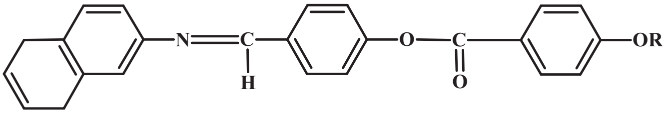
Series-A



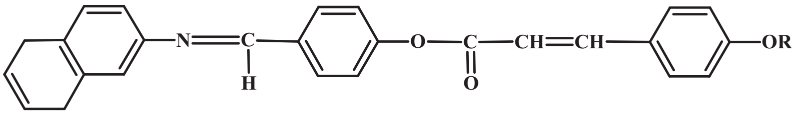
Series-B



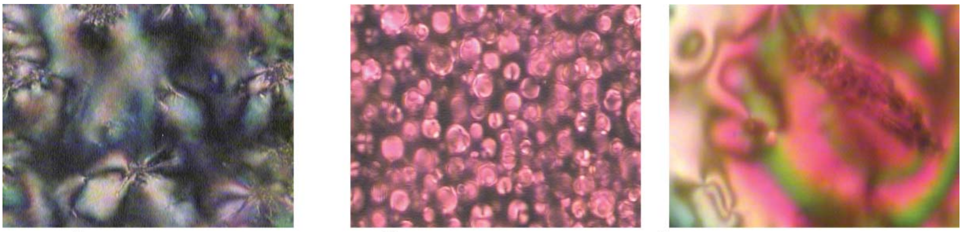
Series-I



Series-II



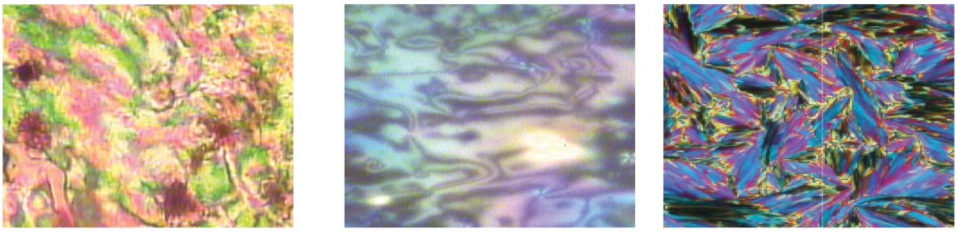
Series-III



A_5 Nematic phase at 142.3°C

B_5 Nematic phase at 142.6°C

A_{14} Nematic phase at 76.5°C



A_{14} SmC phase at 66.9°C

B_{14} Nematic phase at 122.5°C

B_{14} SmC phase at 101.8°C

Figure 5. Microphotograph of liquid crystalline compound.

Table 4 indicates that the nematic and smectic thermal stability of Series-II are higher by 64.0°C and 33.4°C, respectively, than that of present Series-A. Similarly Series-III members are higher by 25.2°C and 22.6°C, respectively, than those of novel Series-B. Both the series differ only at one terminus. Series-A and -B have a 6-fluorobenzothiazole ring at the terminus instead of the naphthalene ring of Series-II and -III. Compared with molecules of Series-II and -III, the molecules of Series-A and -B are more polarizable, but have increased breadth due to the 6-fluorobezothiazole moiety.

Gray [6] has explained that the increase in the breadth of the molecules reduces both nematic and smectic thermal stabilities. In the Series-II and -III, the effect of breadth is not so prominent, due to the 2-substitution in the naphthalene nucleus of the molecules, making them linear. Therefore, probably both the smectic and nematic thermal stabilities are higher in the Series-II and -III.

All the compounds of Series-A and -B exhibit mesomorphism. On cooling the isotropic liquid of Series-A, compounds formed small droplets that coalesce to classical Schlieren textures characteristic of the nematic phase. On further cooling, the higher members show a focal-conic texture characteristic of the SmC mesophase. For Series-B on cooling the isotropic liquid, all the members exhibit the Schlieren texture of the nematic phase; on further cooling, *n*-octyloxy to *n*-octadecyloxy members exhibit an enantiotropic SmC phase. The results are consistent with the assignment of each mesophase type using the classification system reported by Sackmann and Demus [29] and Gray and Goodby [30]. The textures of A_5,A_{14},B_5, and B_{14} are shown in Fig. 5.

4. Conclusion

In this paper, we have reported the synthesis and characterization of two new mesogenic homologous series viz 6-fluoro 2-[4-(4′-*n*-alkoxybenzoyloxy) benzylidenamino] benzothiazole (Series-A), which contains an ester-azomethine central linkage, and 6-fluoro 2-[4-(4′-*n*-alkoxy cinnamoyloxy) benzylidenamino] benzothiazole (Series-B), which contains a cinnamate-azomethine central linkage. Series-A with an ester-azomethine central linkage has lower thermal stabilities compared with Series-B with a cinnamate-azomethine central linkage. The mesophase range of novel Series-B is higher than that of novel Series-A that has been attributed to the high polarizability of the molecule of Series-B with a cinnamoyloxy central linkage, which are more stable as compared with the Series-A containing ester-azomethine central linkage due to greater molecular length and polarizability of the molecule resulting from additional –CH=CH– units in the central linkage.

Acknowledgment

We thank Gujarat Narmada Valley Fertilizer Company Ltd. (G.N.F.C.), Bharuch for providing facilities of elemental analysis, Atul Industries Ltd. Atul. for DSC analysis, and we also thank SAIF Chandigarh for providing facilities of FT-IR, ^{1}H-NMR, ^{13}C-NMR, and Mass spectral analysis.

References

[1] Thaker, B. T., Patel, B. S, Solanki, D. B., Dhimmer, Y. T., & Dave, J. S. (2010). *Mol. Cryst. Liq. Cryst.*, *517*, 63.
[2] Balkwill, P., Bishop, D., Pearson, A., & Sage, I. (1985). *Mol. Cryst. Liq. Cryst.*, *123*, 1.
[3] Hird, M., Gray, G. W., & Toyne, K. J. (1992). *Liq. Cryst.*, *11*, 531.
[4] Beguin, A., & Dubois, J. C. (1979). *J. Phys.* (Paris), *40C*, 9.
[5] Wen, J., Xu, Y., & Chen, Q. (1994). *J. Fluorine Chem.*, *66*, 15.
[6] Gray, G. W., Hird, M., Lacey, D., & Toyne, K. J. (1989). *J. Chem. Soc., Perkin Trans II*, 2041.
[7] Clark, N. A., & Lagerwall, S. T. (1980). *Appl. Phys. Lett.*, *36*, 899.
[8] Bone, M. F., Coates, D., Gray, G. W., Lasey, D., Toyne, K. J., & Young, D. J. (1986). *Mol. Cryst. Liq. Cryst.*, *3*, 189.
[9] Yoshino, K., Ozaki, M., Taniguchi, H., Ito, M.; Satoh, K., Yamasaki, N., & Kitazume, T. (1987). *Japan J. Appl. Phys.*, *26*, L77.
[10] Saito, S., Murashiro, K., Kikuchi, M., Demus, D., Inukai, T., Neundorf, M., & Diele, S. (1993). *Ferroelectrics*, *147*, 367.
[11] Sakaigawa, A., & Nohira, H., (1993). *Ferroelectrics*, *71*, 1478.
[12] Kauffman, J. M., & Bajwa, G. S. (1993). *J. Heterocy. Chem.*, *30*, 1613.
[13] So, Y. H., Zaleski, J. M., Murlick, C., & Ellaboudy, A. (1996). *Macromolecules*, *29*, 2783.
[14] Weisswange, W. (1925). PhD thesis, University at Halle, Germany.
[15] Belmar, J., Parra, M., Zuniga, C., Perez, C., & Munoz, C. (1999). *Liq. Cryst.*, *26*, 389.
[16] Tanaka, K., Kumagai, T., Aoki, H., Deguchi, N., & Iwata, S. (2001). *J. Org. Chem.*, *66*, 7328.
[17] Costa, T. M. H., Stefani, V., Gallas, M. R., Balzaretti, N. M., & Da Jornada, J. A. H. (2001). *J. Mater. Chem.*, *11*, 3377.
[18] Pavluchenko, A. I., Smirnova, N. I., Titov, V. V., Kovahev, E. I., & Djumaev, K. M. (1976). *Mol. Cryst. Liq. Cryst.*, *37*, 35.
[19] Matsui, M., Kamino, Y., Hayashi, M., Funabiki, K., Shibata, K., Muramatsu, H., & Kaneko, M. (1998). *Liq. Cryst.*, *25*, 235.
[20] Dave, J. S., & Vora, R. A. (1970). Mesomorphic behaviour of the cholesteryl esters-I: p-n-alkoxybenzoates of cholesterol. In: J. F. Jonson & R. S. Porter (Eds.), *Liquid Crystals and Ordered Fluids*, Plenum Press: New York, p. 477.
[21] Gray, G. W., & Jones, B., (1953). *J. Chem. Soc.*, 4179.
[22] Pinol, R., Ros, M. B., Serrano, J. L., & Sierra, T. (2004). *Liq. Cryst.*, *31*, 1293.
[23] Guillevic, M. A., & Dvancanw, B. (2000). *Liq. Cryst.*, *27*, 153.
[24] Collings, P. J., & Hird, M. (1998). *Introduction to Liquid Crystals: Chemistry and Physics*. Taylor & Francis: London.

[25] Berdague, P., Bayle, J. P., Ho, M. S., & Fung, B. M. (1993). *Liq. Cryst.*, *14*, 667.

[26] Ha, S. T., Koh, T. M., Yeap, G. Y., Lin, H. C., Ling, L. S., Win, Y. F. & Ong, S. T. (2010). *Mol. Cryst. Liq. Cryst.*, *528*, 10.

[27] Vora, R. A., & Prajapati, A. K. (1998). *Liq. Cryst.*, *25*, 567.

[28] Prajapati, A. K., Thakkar, V., & Bonde, N. (2003). *Mol. Cryst. Liq. Cryst.*, *393*, 41–48.

[29] Sackmann, H., & Demus, D. (1966). *Mol. Cryst. Liq. Cryst.*, *2*, 81.

[30] Gray, G. W., & Goodby, J. W. (1984). *Smectic Liquid Crystals: Textures and Structures*. Leonard Hill: Glasgow and London.